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Puncture Self-healing Polymers for Aerospace Applications

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Introduction

Space exploration launch costs on the order of $10K per pound provide ample incentive to seek innovative, cost-effective ways to reduce structural mass without sacrificing safety and reliability. Damage-tolerant structural systems can provide a route to avoiding weight penalty while enhancing vehicle safety and reliability. Self-healing polymers capable of spontaneous puncture repair show great promise to mitigate potentially catastrophic damage from events such as micrometeoroid penetration. Effective self-repair requires these materials to heal instantaneously following projectile penetration while retaining structural integrity.

Poly(ethylene-co-methacrylic acid) (EMMA), also known as Surlyn is an ionomer-based copolymer that undergoes puncture reversal (self-healing) following high impact puncture at high velocities.[1,2] However EMMA is not a structural engineering polymer, and will not meet the demands of aerospace applications requiring self-healing engineering materials. Current efforts to identify candidate self-healing polymer materials for structural engineering systems are reported. Rheology, high speed thermography, and high speed video for self-healing semi-crystalline and amorphous polymers will be reported.

Experimental

Materials. Surlyn 8940 (Dupont), Affinity EG8200G (Entec resins), and Lexan (GE) samples were provided by their respective manufacturers/distributors. Poly(butylene terephthalate) (PBT), and poly(butylene terepthalate)-co-poly(alkylene glycol terepthalate) (PBT-co-PAGT) and poly(butadiene)-graft-poly(methyl acrylate-co-acrylonitrile) (PB-g-PMA-co-A)were purchased from Sigma-Aldrich Company and used as received.

Instrumentation. The thermal properties of the polymers were characterized by Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA). DMA was also utilized to obtain molecular relaxations in polymers studied. All experimental data were collected using a TA Instruments DMA Q800 dynamic mechanical analyzer and a single cantilever clamp. Mechanical properties were also assessed by Sintech 2W instron according to ASTM D638 at crosshead speeds of 5.08 mm/min. Rheometry was utilized to obtain viscosity and melt flow properties of the polymers at various temperatures.

Ballistics Testing. Ballistic testing was conducted to obtain dynamic damage measurements for the polymers to characterize self-healing capability. The 7.6 cm x 7.6 cm x 4.9 mm panels of the different materials were prepared and ballistic testing was performed at various temperatures. The panels were shot with a .223 caliber semiautomatic rifle from a distance of 23 meters at a local gun range. Panels were either mounted on a tripod or clamped inside an oven for ballistics testing. The .223 caliber rounds were utilized due to their velocity uniformity properties. Remington full metal jacket (copper) 5.56 X 45 mm, 55 grain ammunition was used in these studies. Full Metal Jacketed bullets were the ammunition of choice because their shape and penetration properties mimic micro-meteoroid debris more closely than hollow point bullets. Chronographs were used to measure initial and final bullet velocity. Samples were mounted on either a 1.2 m tripod or from inside an oven with a 7.6 cm diameter hole cut out on two sides.

High Speed Video, High Speed Thermography, and Rheology. Temperatures at the site of impact were measured using a High Speed FLIR ThermaCam sc600 thermal camera. High speed thermography was utilized to obtain temperature and time at the site of impact. A Vision Research model Phantom 9 high speed video camera with a frame rate of 24,092 and a model Phantom 12 high speed video camera with a frame rate of 100,000 frames per second were used to capture high speed video footage of the ballistics testing. The footage was utilized to obtain bullet velocities, rates of healing, and healing mechanisms.

Results and Discussion

Survey of Commercially Available Polymers. Figure 1 illustrates the puncture healing concept. Puncture healing in these materials is dependent upon how a polymer's viscoelastic properties respond to the energy input resulting from the puncture event. Projectile penetration raises the temperature in the vicinity of the impact. Self-healing behavior occurs following puncture, whereby energy must be transferred to the material during impact both elastically and inelastically, thus establishing two requirements for puncture healing to occur: a) The puncture event must produce a local melt state in the polymer material and b) The molten material has to have sufficient melt elasticity to snap back and close the hole.[1,2] Previous ballistic testing studies revealed that Surlyn materials warmed up to a temperature of ~98°C during projectile puncture (3°C higher than its melting temperature).[1,2] The temperature increase produces a localized flow state and the melt elasticity to snap back thus sealing the hole.

Table 1 lists the commercially polymers studied here, together with their physical properties. The polymers were selected based on chemical structure, tensile strength, tensile modulus, glass transition temperature, melting temperature, and impact strength. Surlyn and Affinity EG8200G, both poly(ethylene) based copolymers, self-healed upon ballistic testing at ambient temperature (~24°C).[3] Lexan, poly(butylene terephthalate) (PBT), and poly(butylene terepthalate)-co-poly(alkylene glycol terepthalate) (PBT-co-PAGT) polymers did not display self-healing upon ballistics testing when shot at approximately 25°C. However, these polymers displayed an improvement in damage tolerance upon ballistics testing at elevated temperatures (> 100°C). Poly(butadiene)-graft-poly(methyl acrylate-co-acrylonitrile) (PB-g-PMA-co-A) also displayed much improved healing when tested at 50°C and 100°C.[4]

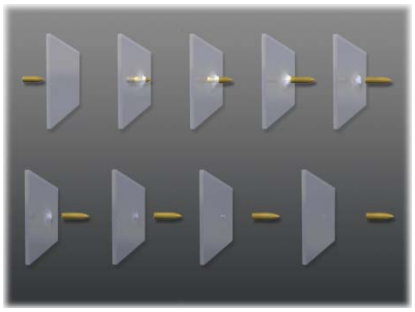

Figure 1: Bullet Penetration Schematic Diagram

Polymer	Tg (°C)	Tm (°C)	Test Temp (°C)	Elongation (%)	Tensile Strength (MPa)	Tensile Modulus (MPa)
Surlyn	-100	54,95	25	120.9	39.6	280.2
Affinity EG 8200G	-68	39,53,75	25	1170	8.0	5.6
PB-g-PMA-co-A	85	-	25,50,100	7.5	37.3	2472.5
Lexan	150	-	25, 100	4.1	52.0	2126.9
PBT	70	210	25, 100	6.5	55.0	1241.0
PBT-co-PAGT	66	180	28	431.6	26.6	388.3

Table 1: Physical Properties of Polymers

High Speed Video, High Speed Thermography, and Rheology

To gain a better understanding of the enhancement of puncture healing functionality in the panels, a thermal imaging camera and high speed video recording camera were employed. A High Speed FLIR ThermaCam sc600 was used to monitor the local material at the puncture site as it heats up to the molten state upon impact. Figure 2 is a thermal image of a panel immediately after being shot. Previous ballistic testing studies conducted by Kalista and co-workers revealed that Surlyn materials warmed up to a temperature of ~98°C during projectile puncture.[1,2] However, it was observed in our studies that in Surlyn and PB-g-PMA-co-A panels, the local material at the puncture site warmed up by a measured average ΔT temperature of 215°C (Shown in Table 2). The discrepancy in site of impact temperatures can be explained as the result of the use of thermal imaging camera's with very different resolution and the use of different experimental conditions i.e. sample

thickness and projectile type, and projectile velocity. Nonetheless, this evidence would further support the explanation for self-healing observed in Surlyn 8940, Affinity EG8200, and PB-g-PMA-co-A and non self-healing in Lexan, PBT, and PBT-co-PAGT. The site of impact temperature in these panels are higher than the glass transition and melting temperatures for each of the respective polymers thus fulfilling the requirement for the puncture event to produce a local melt state in the polymer material to allow self-healing. Lexan, PBT, and PBT-co-PAGT have melting temperatures of at least 200°C, which are higher than or comparable to the increase of temperature experienced at the site of impact for puncture healing polymers.

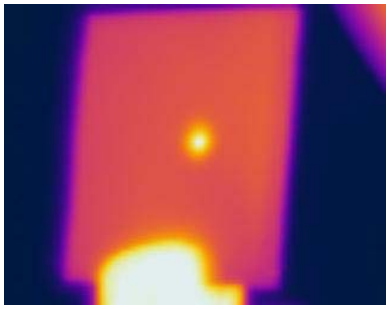

Figure 2: Thermal image of self-healing panel immediately after projectile penetration

High speed video recording was used to capture footage of the puncture healing mechanism at the puncture site during a ballistics test conducted at various temperatures for both Surlyn and PB-g-PMA-co-A. Figure 1 is an illustration of the hypothesized healing process of a polymer panel as a projectile passes through it. The proposed mechanism of self-healing was confirmed and validated with high speed video capturing the healing process after projectile puncture at the site of impact in Surlyn panel at a frame rate of 100,000 frames per second and at a test temperature of 15°C. The self-healing process in Surlyn was observed to be on the order of microseconds. The self-healing process for PB-g-PMA-co-A was captured with high speed video at a frame rate of 24,092 frames per second and at a temperature of approximately 50°C. Despite complete healing of the puncture site in the panel shot at 50°C, high speed video disclosed that a small percentage of material was released at the puncture site during impact and penetration. A loss of material on impact will decrease the amount of material available to heal the puncture site at the time of penetration. This explains why self-healing is not observed for the PB-g-PMA-co-A panels at temperatures below 50°C despite the heating of the local material at the puncture site to temperatures in excess of 100°C from friction caused by projectile penetration. It is also explains why self-healing in the PB-g-PMA-co-A panels improve with increasing temperature, since the polymer lacks the elasticity and chain mobility at lower temperatures, to effectively elongate with projectile passage partially or fully thus resulting in a loss of polymer material. Instead of parting the polymer material, the projectile pushes away or carries polymer material with it. At temperatures below 50°C, more material is lost at time of impact, thus decreasing the amount of material available to seal the puncture.

Table 2: Rheology with Thermal data for Surlyn and PB-g-PMA-co-A

Polymer	T_g(°C)	T_m(°C)	T(°C) at site of impact	Viscosity at T(°C), Eta*, (Poise)
Surlyn	-100	95	240	3282
PB-g-PMA-co-A	85	--	265	4333

Rheology was performed to correlate melt flow properties of local material at the site of impact as the self-healing material undergoes thermal transitions due to friction induced increases in temperature. Surlyn and PB-g-PMA-co-A exist as solid, tough polymers at ambient temperatures ~ 25°C. Specific heats were obtained in the temperature range of 25°C -220°C for Surlyn and PB-g-PMA-co-A. Transitions for Surlyn occur at -100°C and 95°C. Transitions occur at 85°C for PB-g-PMA-co-A. Both polymers maintain relative stiffness despite being above their respective glass transition temperatures. Between the temperature range of 25°C – 220°C the materials change from a glassy phase to viscous flow phase, in part due to a second set of thermal transitions. Surlyn has a melting temperature at 95°C and PB-g-PMA-co-A exhibits a glass transition at 85°C. However, both polymers do not begin to flow until much higher temperatures. At 25°C, both exist as glassy, tough polymers. At respective site of impact temperatures, 240°C for Surlyn and 265°C for PB-g-PMA-co-A, melt viscosities of both Surlyn and PB-g-PMA-co-A were recorded at 3282 and 4333 Poise, respectively (as shown in Table 2). At these temperatures, both polymers behave as viscous liquids. As these materials are shot and the bullet penetrates, an increase in temperature is observed at the site of impact. Each material experiences a temperature increase of ~215°C at the site of impact. The materials possessing self-healing functionality go from a glassy state to viscous flow phase as the temperature at the site of impact increases past each material's melting temperature. As the materials cool, the local material around the penetration site goes from viscous liquid back to a glassy state, while molten material flows to close the hole at the site of impact. The morphologies of the two polymers appear to have no direct influence on the healing process. Healing after puncture appears to be achievable for both amorphous and semi-crystalline polymers. The healing process appears to more driven by ΔT at the site of impact in relation to melting temperatures and melt flow properties at a particular temperature, rather than morphology.

Conclusions

Several commercially available polymers possessing unique puncture self-healing functionality at low to mid range temperatures with similar and better mechanical properties than Surlyn have been identified. Puncture healing functionality is possible in both semi-cyrstalline and amorphous polymers. High speed thermography revealed a ΔT = 215°C at the site of impact for both Surlyn and PB-g-PMA-co-A polymers. Puncture self-healing was more effective when site of impact temperatures were above the glass transition temperatures and melting temperatures of respective polymers. Puncture self-healing improved with increasing temperature for the commercially available polymer, PB-g-PMA-co-A. The puncture healing mechanism of a pair of self-healing polymer panels was captured and confirmed with high speed video. Melt viscosities of both Surlyn and PB-g-PMA-co-A were recorded at 3282 and 4333 Poise, respectively (as shown in Table 2) at temperatures comparable to temperatures observed at the site of impact following bullet penetration.

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